

Sodium-Ion Nanomachining to Shape Microcrystals into Nanostructures and Tune Their Properties

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1. Supplementary Figures

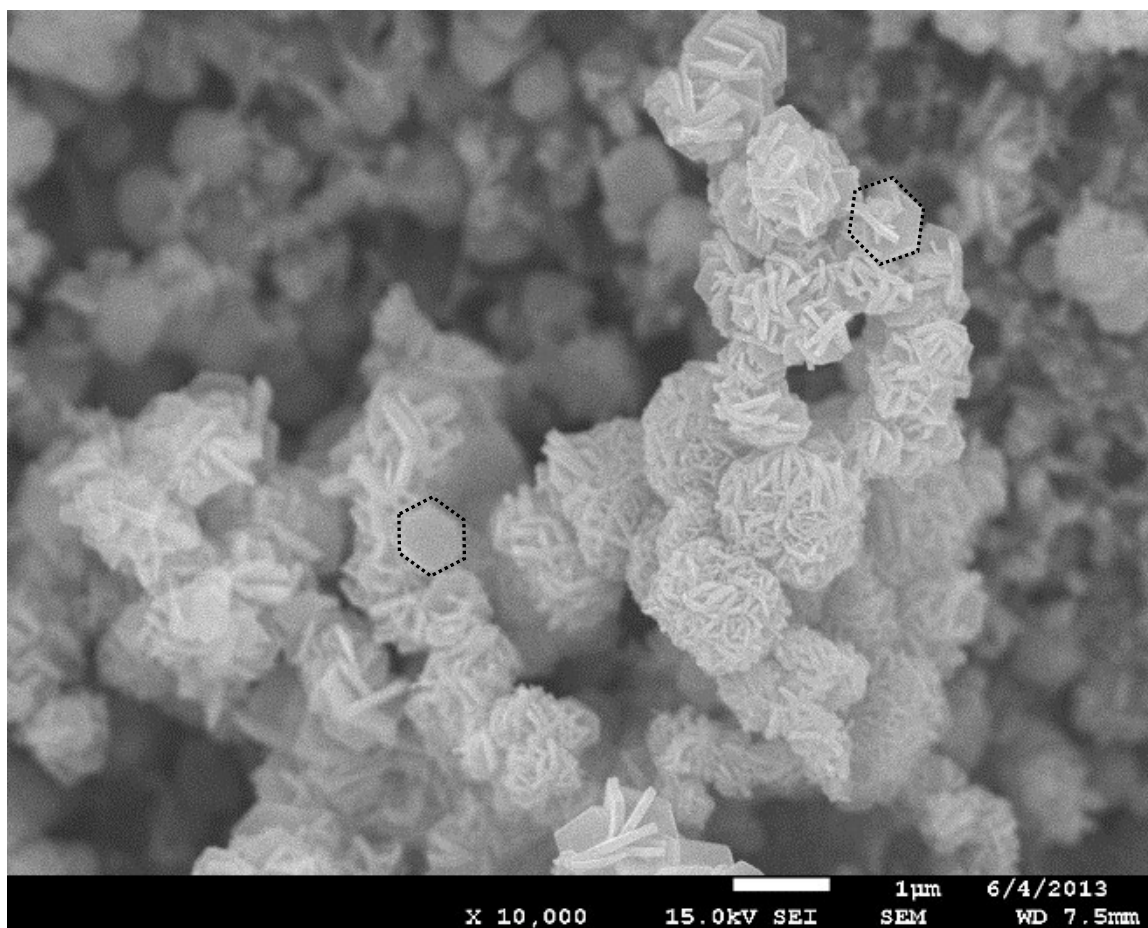


Figure S1. A presentative low-magnification image showing the overall morphology of the hierarchical structures obtained by Na-ion ECNM. The hexagonal frames highlight two representative nanopetal building units.



Figure S2. A presentative TEM image showing the basic hexagonal nanopetals with various tilted at various degrees on the TEM grid. The dash lines are provided to easy see the outline of the hexagonal structure of those nanopetals.

The EDS analysis of as-prepared flower-like hierarchical structures shows that the ratio of Fe:O was close to ~2:3 (Figure S3a), which matches that of Fe₂O₃. The Fe 2p narrow scan X-ray photoelectron spectroscopy (XPS) spectrum matches the typical spectrum of Fe³⁺ in α-Fe₂O₃, with two photoelectron peaks appeared at ~724.37eV (Fe 2p_{1/2}) and ~710.75eV (Fe 2p_{3/2}) and characteristic shakeup satellite peak appeared at ~718.8eV (Figure S3b).^{1,2} No photoelectron peak of metallic iron at ~706.8eV (Fe 2p_{3/2}) was detected, indicating that no metallic iron (or very trace amount which cannot be detected by XPS) was left after the reversible reaction: 2Fe⁰ + 3Na₂O ↔ α-Fe₂O₃ + 6Na⁺ + 6e⁻ and the final flower-like product after cycling is Fe₂O₃. The Raman and XRD analysis also double confirmed the chemical composition is α-Fe₂O₃, with all the characteristic peaks identified (Figure 3Sc,d).

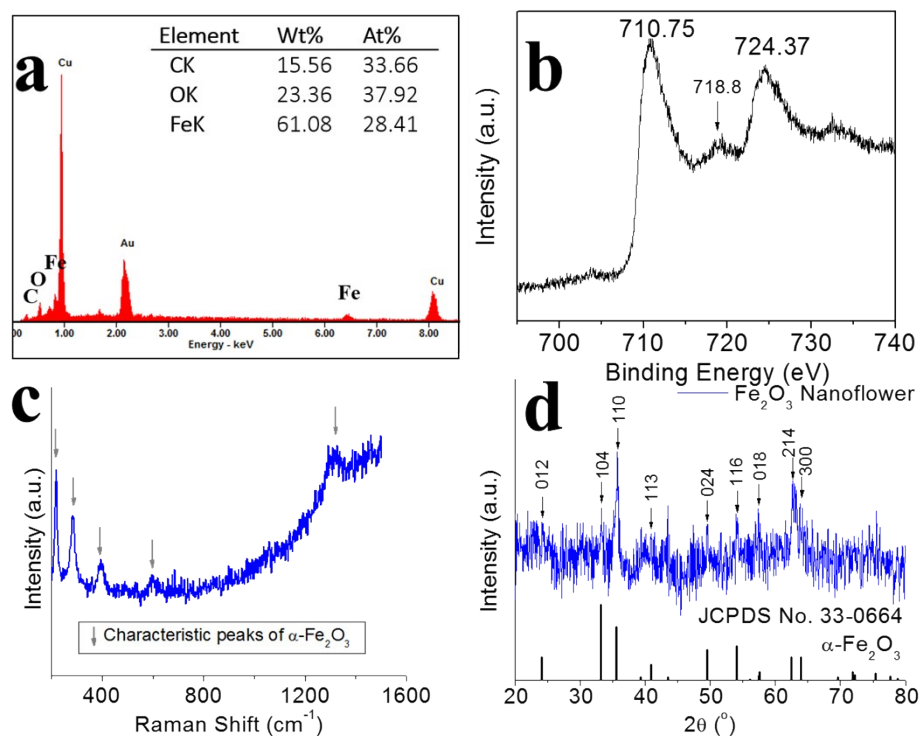


Figure S3. The as-derived flower-like α-Fe₂O₃ was extensively characterized: (a) EDS; ~15wt % of carbon in EDS comes from super P additive; (b) Fe 2p narrow scan X-ray photoelectron

spectroscopy (XPS) spectrum; photoelectron peaks ~ 724.37 eV and 710.75 eV can be assigned to Fe $2p_{1/2}$ and Fe $2p_{3/2}$ and peak at ~ 718.8 eV is a characteristic shakeup satellite peak for Fe(III) species; (c) Raman Spectrum and (d) X-ray diffraction (XRD), and all the Raman peaks (marked by grey arrows) and XRD peaks (marked by black arrows) can be assigned to α - Fe₂O₃.

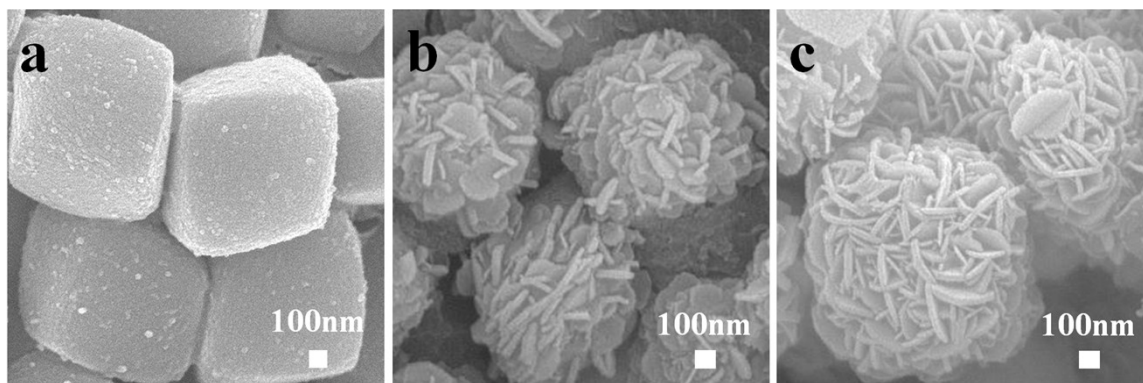


Figure S4. Effects of number of cycles: Selected SEM images to show the effect of the number of cycles on the morphology evolution of the particles under typical sodium-ion nanomachining conditions: (a) precursor rhombohedral particles, (b) small amount of nanopetals carved on the surface after 10 cycles; (c) large amount of nanopetals carved on the surface after 120 cycles.

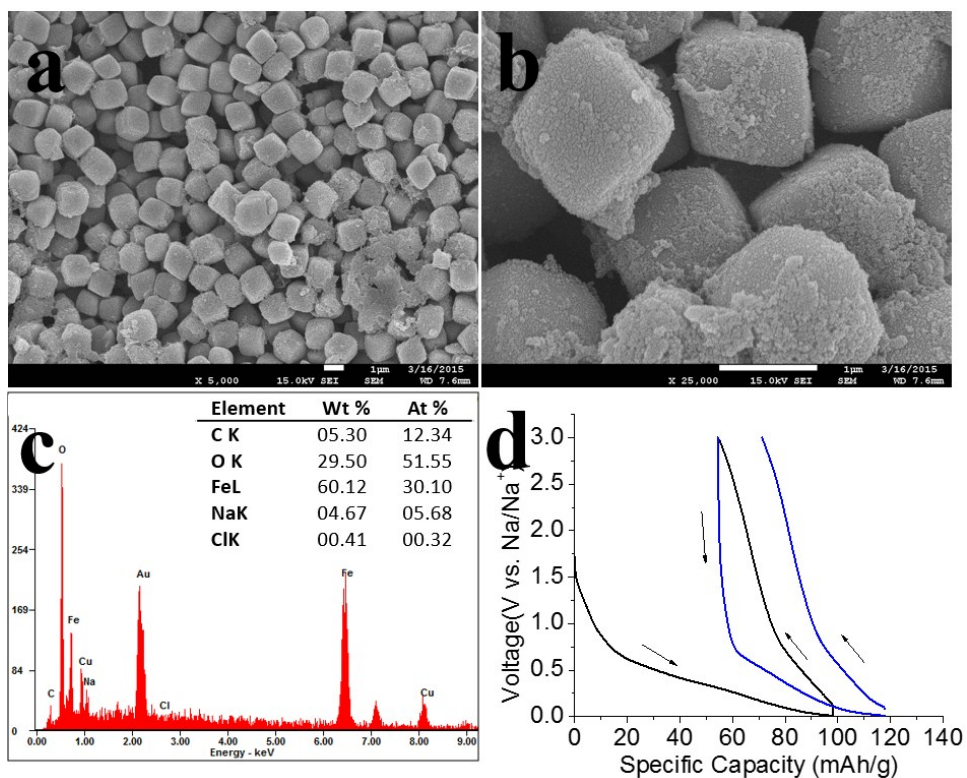


Figure S5. Effects of carbon black selected: (a, b) FESEM images and (c) EDS of α -Fe₂O₃ & Super C65 instead of α -Fe₂O₃ & Super P after Na-carving process for 120 times at 200 mA/g;

carbon in EDS comes from Super C65 additive, Na and Cl come from electrolyte residue. (d) First two cycle charge-discharge profiles.

Interestingly, it is found that the carving process is also sensitive to the composition of the active layer. When Timcal C-ENERGY™ Super C65 was used to substitute Timcal Super P, the nanoflower structure can no longer be obtained.(Figure S5a-b). The molar ratio of O:Fe in the derived product is little higher around 1.7:1 (Figure S5c) and charge-discharge profiles are similar(Figure S5d). The distinct difference between Super C65 and Super P is the total Fe content of Super C65 is 5 ppm, or 2.5 times higher than that of Super P. It is possible that Fe in conductivity enhancer, together with Fe in Fe₂O₃, also can significantly affect the Na-carving process, probably due to the Fe can also get involved in the reaction: $\alpha\text{-Fe}_2\text{O}_3 + 6\text{Na}^+ + 6\text{e}^- \leftrightarrow 2\text{Fe}^0 + 3\text{Na}_2\text{O}$. Further investigation is on-going to gain better understanding about the effects of carbon black selected.

References

- (1) Yao, X.; Tang, C.; Yuan, G.; Cui, P.; Xu, X.; Liu, Z. *Electrochem. Commun.* **2011**, *13*, 1439.
- (2) Xiong, Q. Q.; Tu, J. P.; Ge, X.; Wang, X. L.; Gu, C. D. *J. Power Sources* **2015**, *274*, 1.